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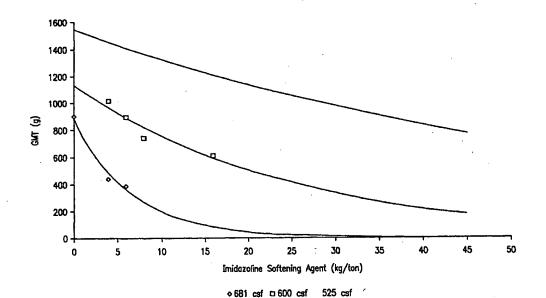
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### (54) Title: HIGHLY SUBSTANTIVE SOFT TISSUE



(57) Abstract: The present invention is generally directed to cellulosic tissues having excellent softness and strength. The tissues are made from a multi-layered paper web containing outer layers made from fibrillated fibers and/or a blend of low-average length and high-average length fibers. The paper web is applied with a softening agent for producing a web having reduced levels of fiber bonding. Moreover, a bonding agent is also applied to the web to improve strength and tear resistance.

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# HIGHLY SUBSTANTIVE SOFT TISSUE Background of the Inventi n

Absorbent paper products such as paper towels, facial tissues and other similar products are designed to include several important properties. For example, the products should have good bulk, a soft feel and should be highly absorbent. The product should also have good strength, even when wet, and should resist tearing. Unfortunately, it is very difficult to produce a high strength paper product that is also soft. Usually, when steps are taken to increase one property of the product, other characteristics of the product are adversely affected.

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For instance, strength is typically increased by the addition of certain strength or bonding agents to the product. Although the strength of the tissue product is increased by such bonding agents, the resulting tissue product is generally not soft. As a result, various softening agents can be applied to the tissue product to reduce fiber bonding within the paper product and thereby increase softness.

However, by reducing fiber bonding with a softening agent, the strength of the tissue product is also significantly reduced. In particular, when applied, softening agents often cause excessive "debonding" and compete with conventional strength agents for bonding sites. As such, most tissues can only accommodate limited amounts of a softening agent. Moreover, even when applied at such limited amounts, the softening agent can nevertheless result in a much weaker tissue product due to the displacement of some of the bonding agent from the bonding sites. This weaker tissue product can exhibit substantial amounts of lint and slough production.

As such, a need currently exists for a tissue product that is soft, but also possesses sufficient strength. In particular, a need currently exists for a tissue product that can be applied with a softening agent without adversely affecting the strength characteristics of the tissue so that

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t aring, lint production, and/or slough is not significantly increased.

### Summary of th Inv ntion

The present invention is directed to providing a tissue made from a multi-layered paper web having two outer layers. In general, the outer layer(s) can be made from a variety of fibrous materials. For example, in one embodiment, various cellulosic fibers, such as softwood fibers, hardwood fibers, etc., can be utilized in the outer layer(s).

According to the present invention, the outer layer(s) are configured to have an increased number of bonding sites to accommodate sufficient amounts of more than one additive. A bonding site generally refers to various substituents located on a fiber, such as hydroxy groups, that are capable of bonding to an additive. To increase the number of bonding sites, any of a variety of mechanisms can be utilized. In one embodiment, the outer layer(s) contains some high-average length fibers (i.e., generally greater than about 1.2 mm) that are fibrillated. Fibrillation can provide an increase in the surface area of a fiber, thereby providing an increased number of sites for bonding to an additive, such as a bonding or softening agent. In some embodiments, the high-average length fibers are fibrillated to an extent such that the resulting fibers have a Canadian Standard Freeness ("CSF") (TAPPI T227m-58) between about 400 to about 800, and more particularly, between about 500 CSF to about 700 CSF.

In another embodiment, the outer layer(s) can also contain a blend of high-average length fibers (fibrillated or un-fibrillated) and low-average length fibers (i.e., generally less than about 1.2 mm). Similar to fibrillation, a blend of differently sized fibers can also provide an increased number of bonding sites in accordance with the present invention. When utilized, low-average length fibers can generally be incorporated into the outer layer(s) in any desired amount. Typically, a fiber blend used in an outer layer of the present invention contains about 50% to about 95% by weight

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of low-average length fibers, and more particularly between about 60% to about 90%.

By providing an increased number of bonding sites, various additives, such as bonding and softening agents, can be applied to the outer layer(s) of a tissue of the present invention without substantially competing with each other for the same bonding sites. As such, a tissue of the present invention can be applied with higher levels of a softening agent without adversely affecting the strength of the tissue and without causing substantial lint and slough production. As used herein, the term "slough" generally refers to the wearing away of any part of the tissue by rubbing the tissue against a surface.

For instance, a tissue made according to the present invention can be applied with a softening agent in an amount from about 1 kilogram per metric ton of fiber weight (kg/MT) to about 60 kg per metric ton of fiber weight, and more particularly between about 10 kg/MT to about 35 kg/MT, without resulting in substantial lint or slough. Moreover, it has also been discovered that the tissue can retain at least about 75% of the softening agent, and more particularly between about 80% to about 96% of the softening agent, without having substantial increases in slough or lint production.

A tissue of the present invention can generally be formed according to a variety of papermaking processes known in the art. In particular, any process capable of forming a multi-layered paper web can be utilized in the present invention. For example, a papermaking process of the present invention can utilize creping, embossing, wet-pressing, through-drying, through-dry creping, uncreped through-drying, double creping, as well as other steps in forming the multi-layered paper web.

Various features and aspects of the present invention are discussed in greater detail below.

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### Bri f D scripti n f th Drawings

A full and enabling disclosure of the present invention, including the best mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figures in which:

Figure 1 is a graphical representation of geometric tensile strength (GMT) versus the add-on level of a softening agent for various embodiments of the present invention in which the paper web comprises fibers that have been fibrillated for 0 minutes, 6 minutes, and 12 minutes; and

Figure 2 is a graphical representation of geometric tensile strength (GMT) versus the add-on level of a softening agent for various embodiments of the present invention in which the paper web comprises a blend of eucalyptus fibers and "Longlac-19" fibers.

Repeat use of reference characters in the present specification and drawings is intended to represent same or analogous features or elements of the present invention.

### <u>Detailed Description of Representative Embodiments</u>

Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents.

In general, the present invention is directed to tissues having

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improved softn ss and having smooth, low friction surfaces. Moreover, it has been discovered that by producing a tissue having multiple layers in accordance with the present inv ntion, the outer layer(s) can have an increased number of bonding sites. As such, a tissue of the present invention can not only exhibit improved softness, but also retain adequate strength when either dry or wet. Furthermore, because the tissues can retain adequate strength, they generally have low slough and do not produce a substantial amount of lint when used.

As stated, tissues made according to the present invention can generally be formed in a variety of ways. In particular, the tissue can be formed into a single or multi-ply tissue, so long as the tissue contains more than one layer. For example, in one embodiment of the present invention, a single ply tissue can be formed from one multi-layered paper web. In another embodiment, a three-ply tissue can be formed from three single or multi-layered paper webs that are adhesively attached to each other. Normally, the basis weight of a tissue made according to the present invention is from about 10 grams per square meter to about 50 grams per square meter.

When forming a tissue of the present invention, it is typically desired that the tissue have at least three layers. For example, in one embodiment, the tissue can include two outer layers surrounding an inner layer. However, it should be understood that a tissue of the present invention need not comprise three layers. In fact, any number of layers can be utilized as long as the resulting tissue has at least two outer layers.

As stated, a tissue of the present invention typically includes two outer layers that surround at least one inner layer. In general, an outer and/or inner layer of the tissue can be formed from any of a variety of materials. In particular, a variety of natural and/or synthetic fibers can be used. For example, some suitable natural fibers can include, but are not to, nonwoody fibers, such as abaca, sabai grass, milkweed floss fibers,

pineapple leaf fibers; softwood fibers, such as northern and southern softwood kraft fibers; hardwood fibers, such as eucalyptus, maple, birch, aspen, and the like. In addition, furnishes including recycled fibers may also be utilized. Moreover, some suitable synthetic fibers can include, but are not limited to, hydrophilic synthetic fibers, such as rayon fibers and ethylene vinyl alcohol copolymer fibers, as well as hydrophobic synthetic fibers, such as polyolefin fibers.

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In one embodiment, an outer and/or inner layer of the present invention can contain fibers having a "high-average length". As used herein, the phrase "high-average length" generally refers to fibers having an average fiber length greater than about 1.2 mm, and usually from about 1.5 mm to about 6 mm. Illustrative examples of suitable pulps include southern pines, northern softwood kraft pulps, red cedar, hemlock, black spruce, and mixtures thereof. Exemplary commercially available long pulp fibers suitable for the present invention include those available from Kimberly-Clark Corporation under the trade designations "Longlac-19," "Coosa River-54," "Coosa River-56" and "Coosa River-57". For example, in one embodiment, northern softwood kraft fibers can be used to form the inner layer. Northern softwood kraft fibers typically have a fiber length of about 1.8 mm to about 2.5 mm.

In some embodiments, fibers having a "low-average length" can also be utilized in an inner and/or outer layer of the present invention. As used herein, the phrase "low-average fiber length" refers to fibers having an average fiber length of less than about 1.2 mm, usually from about 0.7 mm to about 1.2 mm. Examples of low-average length fibers can include certain grades of virgin hardwood pulp and secondary (i.e., recycled) fiber pulp from sources such as, for example, newsprint, reclaimed paperboard, and office waste. One particular example of fibers having a low-average length suitable for use in the present invention are hardwood fibers, such as eucalyptus fibers, which generally average from about 0.8 mm to about

1.2 mm in length. By utilizing fibers having a low average fiber length, such as eucalyptus fibers, a layer of the present invention can be imparted with certain b neficial properties. For instance, low-average length fibers can provide uniform formation, increased softness, enhanced brightness, as well as increased opacity. Moreover, low-average length fibers, such as eucalyptus fibers, can also change the pore structure of the paper, thereby greatly increasing the wicking ability of the paper web.

In order to strengthen the tissue, various bonding agents (e.g., wetstrength or dry strength agents) can be applied in accordance with the
present invention. Particular bonding agents that may be used include
latex compositions, such as acrylates, vinyl acetates, vinyl chlorides, and
methacrylates. Some water soluble bonding agents may also be used
including polyacrylamides (e.g. glyoxylated polyacrylamides), polyvinyl
alcohols, and carboxymethyl cellulose. In one embodiment, the bonding
agent used in the present invention comprises an ethylene vinyl acetate
copolymer. In particular, the ethylene vinyl acetate copolymer can be
cross-linked with N-methyl acrylamide groups using an acid catalyst.
Suitable acid catalysts include ammonium chloride, citric acid, and maleic
acid.

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Although not required, the bonding agent is generally applied to a layer such that it does not cover the entire layer. In particular, because the bonding agents can adversely affect the absorbency of a paper web, it is generally desired to minimize the amount of bonding agent applied. Thus, according to the present invention, the bonding agent is normally applied to each side of a paper layer so as to cover from about 30% to about 60% of the surface area of the web. More particularly, in most applications, the bonding agent will cover from about 40% to about 50% of the surface area of each side of a layer. The total amount of bonding agent applied to each side of a layer is typically in the range of from about 4% to about 7% by weight, based upon the total weight of the layer. In

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other words, the bonding agent is applied to each side of the web at an add on rate of about 2% to about 3.5% by weight. At these amounts, the bonding agent can penetrate the paper layer from about 25% to about 40% of the total thickness of the web. In most applications, the bonding agent should not penetrate over 50% of the layer but should at least penetrate from about 10% to about 15% of the thickness of the layer.

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In addition, the bonding agent can be applied to a layer in a preselected pattern. In one embodiment, for instance, the bonding agent can be applied in a reticular pattern, such that the pattern is interconnected forming a net-like design on the surface. In an alternative embodiment, however, the bonding agent can be applied to the web in a pattern that represents a succession of boat-shaped dots. Applying the bonding agent in discrete shapes, such as dots, may provide sufficient strength to the layer without covering a substantial portion of the surface area. In some embodiments, the pattern applied to each side of the layer is compressed such that the dots are small and are arranged close together.

Although the application of bonding agents can vastly improve some properties of the tissue, they can also have an adverse affect on other properties. For instance, bonding agents can significantly improve strength and tear resistance, but can undesirably decrease the softness of the tissue.

As such, a tissue of the present invention can be treated with a chemical debonding or "softening" agent to impart a "soft feel" to the tissue product. Some softening agents are also believed to act as lubricants or friction reducers. Generally speaking, a softening agent can be added to the fiber slurry during the pulping process or can be added directly into the head box. Moreover, if desired, a softening agent can also be applied at other stages of the wet-end of a papermaking process or applied directly onto the outer layer(s) of a dried tissue sheet. For

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instance, in one embodiment, discrete surface deposits of the softening agent can be applied to the tissue, as described in U.S. Patent No. 5,814,188 to <u>Vinson</u>, et al., which is incorporated herein in its entirety by reference thereto.

Any material having an affinity to fibers and that is capable of enhancing the soft feel of a tissue product can generally be used as a softening agent in the present invention. For instance, the softening agents of the present invention can be cationic, amphoteric, and can be a variety of combinations thereof, to facilitate bonding to the fibers of a tissue layer. Moreover, various non-ionic softening agents can also be utilized, particularly when used in conjunction with cationic and/or amphoteric softening agents. Examples of suitable softening agents can include, but are not limited to, quaternary ammonium compounds, imidazolinium compounds, bis-imidazolinium compounds, diquaternary ammonium compounds, polyquaternary ammonium compounds, phospholipid deriviatives, polydimethylsiloxanes and related cationic and non-ionic silicone compounds, fatty & carboxylic acid derivatives, monoand polysaccharide derivatives, polyhydroxy hydrocarbons, etc.

Some specific examples of suitable softening agents are given below:

 Quaternary ammonium compounds having the following basic structure:

$$\left[\begin{array}{c} \stackrel{\stackrel{\scriptstyle \bullet}{\scriptstyle 1}}{\stackrel{\scriptstyle \bullet}{\scriptstyle 1}} \\ \stackrel{\scriptstyle \bullet}{\scriptstyle R_4} \stackrel{\scriptstyle \bullet}{\longrightarrow} \stackrel{\scriptstyle \bullet}{\scriptstyle R_2} \end{array}\right] \qquad X$$

Wherein

X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

R1 can be hydrogen, C1 - C6 alkyl or hydroxyalkyl; and R2, R3, R4 can be the same or different, any lin ar or branched, saturated or unsasturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length;

or

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$$\left[\begin{array}{c} R_1 \\ R_4 \longrightarrow N^{+} \longrightarrow R_2 \\ R_3 \end{array}\right] \qquad X$$

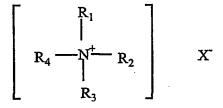
Wherein

X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

R1, R2 can be the same or different, hydrogen, C1 - C6 alkyl or hydroxyalkyl; or R1 can be hydrogen, C1 - C6 alkyl or hydroxyalkyl; R2 can be benzyl or epoxy; and

R3, R4 can be the same or different, any linear or branched, saturated or unsasturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length;

25 or



Wherein

X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible count rion;

R1, R2, R3 can be the same or different, hydrogen, C1 - C6 alkyl or hydroxyalkyl; R4 can be any linear or branched, saturated or unsasturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length;

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2. Quaternary ammonium compounds having the following basic structure:

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$$\left[\begin{array}{c} R_1 \\ R_4 \longrightarrow N^{\pm} \\ R_3 \end{array}\right] \qquad X$$

Wherein

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X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

R1, R2, R3 can be the same or different, hydrogen, C1 - C6 alkyl or hydroxyalkyl; and

R4 are selected from any of the following two groups:

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n=2-6;

m=0-6

p=1-6; and

R5, R6 can be the same or different, any linear or branched, saturated or unsasturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length

10 or

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 $\left[\begin{array}{c} R_1 \\ | \\ R_4 \longrightarrow N^{\frac{1}{2}} \\ R_3 \end{array}\right] \qquad X$ 

Wherein

X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

R1, R2 can be the same or different, hydrogen, C1 - C6 alkyl or hydroxyalkyl; and

R3, R4 can be selected in any combination from the following two groups:

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m=2-6; and

R5 can be any linear or branched, saturated or unsasturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length.

3. Quaternary ammonium compounds having the following basic

structure:

wherein

X= halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

20 R is selected from the following group:

m=2-6; and

R5 can be any linear or branched, saturated or unsaturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic

hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length.

4. Imidazolinium compounds having the following basic structures:

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 $\begin{bmatrix} CH_3 \\ N_+ \\ N_- \\ R_2 \end{bmatrix} X$ 

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X=halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

R1 can be any linear or branched, saturated or unsaturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length; and R2 can be selected from any of the following two groups:

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m=2-6; and

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R5 can be any linear or branched, saturated or unsaturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic

hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length.

5. Bis-imidazolinium compounds having the following basic structure:

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$$\begin{bmatrix} CH_3 & C & CH_2 & CH_3 \\ C & CH_2 & CH_2 & CH_3 \\ C & CH_2 & CH_3 & CH_3 \end{bmatrix}^{++}$$

$$CH_3 & CH_3 &$$

10

### Wherein

X=halide, methyl sulfate, ethyl sulfate, lactate, or other compatible counterion;

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R1, R2 can be the same or different, aliphatic hydrocarbons, linear or branched, saturated or unsaturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, preferably C8 - C30; or R1, R2 can be selected in any combination from any of the following two groups:

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### m=2-6; and

R5 can be any linear or branched, saturated or unsaturated, substituted or non-substituted, with or without ethoxylation, with or without propoxylation, aliphatic hydrocarbon moiety of greater than 8 carbon chain length, preferably between 8 - 30 carbon chain length.

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6. Diquaternary ammonium compounds having the following basic

structure

 $\begin{bmatrix} R_{1} & R_{4} & R_{5} \\ R_{2} & R_{3} & R_{6} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{2} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{3} & R_{6} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{5} & R_{6} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{4} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{++} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5} & R_{5} \\ R_{5} & R_{5} \end{bmatrix}^{+} \times \begin{bmatrix} R_{5}$ 

Wherein

X=halide, methylsulfate, ethylsulfate or other compatible counterion;

10 n=2 - 8;

R, R4 may be the same or different, are H, CH<sub>3</sub>, or (CH<sub>2</sub>)<sub>m</sub>OH where m=1-4;

R2 ,R3 ,R5 ,R6 may be the same or different, are from the following groups:

15

5

(i).  $-(CH_2)_p$  OH, where p=1-6;

or

20

25 where q=1-10, R=aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

or

(iii).

where r=1-10, R'=aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

or

5

10

where s=1-10, t=1-4, R"=aliphatic, C8 - C30, saturated or unsaturated, normal or branched.

7. Polyquaternary ammonium compounds having the following basic structure:

15

$$\begin{array}{c|c}
R_{1} & & & R_{4} \\
R_{2} & & & & R_{5} \\
R_{3} & & & & R_{6}
\end{array}$$

$$\begin{array}{c|c}
R_{4} & & & \\
R_{5} & & & (m+1) X^{-1} \\
R_{6} & & & \\
\end{array}$$

20.

Wherein

X=halide, methylsulfate, ethylsulfate or other compatible counterion;

n=2 - 8;

m=1 or greater;

25

R2, R5 may be the same or different, are aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

or (CH<sub>2</sub>)<sub>q</sub>--CHOH--R' where q=1-6, and R'= aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

or (CH<sub>2</sub>)<sub>r</sub>--O--R" where r=1-6, and R"= aliphatic, C8 - C30, saturated or unsaturated, normal or branched; and

30

R1 ,R4 ,R3 ,R6 may be the same or different, are H, CH<sub>3</sub>, or (CH<sub>2</sub>)<sub>m</sub>OH where m=1-6; or aliphatic, C8 - C30, saturated or unsaturated, normal or branched.

5 8. Phospholipid Derivatives having the following basic structure:

(1)

10 
$$\begin{bmatrix} R_1 \\ R & -N^{+-} & CH_2CHOHCH_2O \end{bmatrix} \xrightarrow{+}_{X} \overset{O}{\longrightarrow}_{X}$$
 (B)y + xA + x

wherein,

x= 1 - 3;

x+y=3;

a=0 - 2;

B=O or OM;

A=an anion;

20 M=a cation;

R, R1, R2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 30 carbon atoms;

or

15

$$\begin{bmatrix} R_1 \\ R & -N^{+} & CH_2CHOHCH_2O \end{bmatrix}_{X}^{+} \stackrel{O}{\underset{P}{\longrightarrow}} (B)y + xA + aM$$

30 wherein x= 1 - 3;

a=0 - 2;

B=O or OM;

A=an anion;

5 M=a cation;

R1, R2 can be the same or different, are alkyl, hydroxyalkyl, carboxyalkyl, C1 - C6, or propoxyalkylene, C1 - C10; or R1, R2 and the nitrogen they are attached to may represent an N-heterocycle; and R has the following structure:

10

15

$$R_4 O \parallel - (CH_2)m - N - C - R_5$$

wherein

m=2 -6;

R4 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons, or cycloalkyl of up to 6 carbons or polyoxyalkylene of up to carbons; and R5 = alkyl, alkenyl, alkoxy or hydroxyalkyl, C5 - C30, or aryl or alkylaryl of up to C30.

20

or

(3)

$$\begin{bmatrix}
R_1 \\
R & -N^{+} & CH_2CHOHCH_2O & -P & OCH_2CHOHCH_2 & -N^{+} & R' \\
R_2 & OM & R_2
\end{bmatrix}$$
2A

30 wherein

A=an anion;

M=a cation;

R; R1, R2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 30 carbons; and

R' has the following structure:

5

wherein

m=2 -6;

10

R4=hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons, or cycloalkyl of up to 6 carbons or polyoxyalkylene of up to carbons; and R6 has the following structure:

15

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} = \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ CH_{3} \end{array} = \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} = \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array}$$

20

where

n ≥ 3;

p= 1-1000; and

q= 1-25.

30

25

Polydimethylsiloxanes and related silicone compounds having the following structures:

Wherein

5 R=alkyl or aliphatic hydrocarbons, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

z= -- alkyl -- O -- alkyl --, alkyl groups having at least 1 carbon; x=alkoxy, halide, methyl sulfate, ethyl sulfate, lactate or other compatible counterion; and

10 n=1 to 50;

or (2)

 $\begin{array}{c}
CH_{3} & CH_{3} & CH_{3} \\
CH_{3} & Si & O & Si \\
CH_{3} & R_{1} & R_{2} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$   $\begin{array}{c}
CH_{3} & CH_{3} \\
CH_{3} & CH_{3}
\end{array}$ 

30 wherein x= 0 to 1000; x, y, z = 1 to 1000; R1, R2 can be the same or different, are alkyl or hydroxyalkyl, C1 - C20 or phenyl;

a= 1-4;

b,c,d=0-20;

Y=halide, methyl sulfate, ethyl sulfate or other compatible counterion; and R can be selected from among the following four groups:

(i).

10

$$R_3 \longrightarrow N^+ \longrightarrow R_5$$

15

20

where

(ii)

R3, R4, R5 can be the same or different, are selected from hydroxyalkyl or alkyl group, C1- C4; or aliphatic group, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

$$R_6 - N^+ - (CH_2)n - N^- - C - R_8$$

30

25

where, R6 = hydroxyalkyl or alkyl C1-C6; or R6, R7, R8 can be the same or different, are selected from aliphatic group, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted; and n=1 -6;

35

or

where

R6, R7 can be the same or different, are alkyl or hydroxyalkyl, C1 - C6;

R8=aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted; and n=1 -6;

or

10 where

R6-hydroxyaikyl or alkyl, C1 - C6;

n=1 -6;

R7=

m=1 - 6; and

20 R9= aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

or

25 where

R6=hydroxyalkyl or alkyl, C1 - C6;

R7=

30

m'=1 - 6; and

R9= aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

(iii)

 $R_{10}$   $N^+$   $R_{11}$ 

10

5

where

R10, R11 can be the same or different, are selected from aliphatic group, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

15 or

R11=

H O
I ||
- (CH<sub>2</sub>)<sub>0</sub> -- N-C-R<sub>12</sub>

20

where

o=1 - 6; and

R12= aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted.

25

(iv) 
$$R_{12} - N + R_{14}$$
  $R_{13}$ 

30

wherein

R12, R13=C1 - C6, alkyl or hydroxyalkyl;

$$R14 = -(CH_2)_0 - C - O - R15;$$

P=1 - 6; and

R15= aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted;

5

or

R12 = C1 - C6 alkyl or hydroxyalkyl;

R13, R14 can be the same or different, and selected from the

10

following two groups:

15

$$\begin{array}{c|c}
 & O \\
 & \parallel \\
 & (CH_2)r - O - C - R_{16} \\
 & (CH_2)s - O - C - R_{17} \\
 & \parallel \\
 & O
\end{array}$$

or

20

25

30

$$-(CH_{2})q' - N - C - R_{18}$$

$$-(CH_{2})s' - N - C - R_{19}$$

$$| | | | | |$$

$$| | | | |$$

$$| | | | |$$

$$| | | |$$

where

r, r', s, s'=0 - 6; and

R16, R17, R18, R19 can be the same or different,

are aliphatic, C8 - C30, normal or branched, saturated or unsaturated, substituted or unsubstituted.

5 or

R12=R13=C1-C6 alkyl or hydroxyalkyl;

R14=

and

10

15

m = 1-6

R15 = C8-C30 aliphatic, normal or branched, saturated or unsaturated, substituted or unsubstituted.

or

(3)

20

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{2} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{2} \\ CH_{3} \\ CH_{4} \\ CH_{4} \\ CH_{5} \\ CH_{5$$

25

30

.

$$R = (CH_{2})_{\Pi} = Si - O = \begin{cases} CH_{3} \\ Si - O \\ CH_{3} \end{cases} = CH_{3}$$

$$CH_{3} = CH_{3}$$

$$CH_{3} = CH_{3}$$

$$CH_{3} = CH_{3}$$

wherein

R=amine, carboxy, hydroxy or epoxy;

n≥3;

. x=1 - 1000;

5 y=1 -25.

or

(4)

10

15

20

 $\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3} & CH_{3} \\ CH_{3} & CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ O & Si \\ CH_{2} \\ CHOH \\ CH_{2} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{2} \\ CH_{3} \\ \end{array} \begin{array}{c} CH_{3} \\ CH_{2} \\ CH_{2} \\ COO \end{array}$ 

Wherein

n=1 - 1000; and

m=1 - 100.

25 or

(5)

5  $CH_3$   $CH_3$ 

Wherein

15 R=alkyl, C1 - C6;

R1=acetate or hydroxy;

n=1 - 100;

m=1 - 100;

x=1 - 1000; and

20 y=1 - 50.

or

(6)

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline \\ CH_3 & Si \\ \hline \\ CH_2 & CH_2 \end{array} \qquad \begin{array}{c} CH_3 \\ \hline \\ O \\ \hline \\ CH_2 \end{array}$$

30 wherein x=1 - 1000; y=1 - 100;

R' has the following structure:

5

and R is selected from the following two groups:

 $(CH_2)a$ 

(Ç<sub>2</sub>H<sub>4</sub>O)b (Ç₃H<sub>6</sub>O)c

 $(C_2H_4O)d$ 

CH<sub>3</sub>

10

(i).

15

20

25

where

Y=halide, methyl sulfate, ethyl sulfate or other compatible counterion;

ΗQ

30

R" = aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

$$a,e = 1-4;$$

b, c, d = 0-20; and b+c+d≥1.

or

(ii).  $CH_3$   $CH_3$   $CH_3$   $CH_2$   $CH_2$   $CH_4$   $CH_4$   $CH_4$   $CH_4$   $CH_4$   $CH_4$   $CH_4$   $CH_4$ 

10

5

15

where

R" = aliphatic, C8 - C30, saturated or unsaturated, normal or branched;

a,e = 1-4;

b, c, d = 0-20; and

b+c+d≥1.

20

10. Fatty and carboxylic acid derivatives having the following structures:

25 
$$RO(C_3H_6O)x(CH_2CH_2O)y - (CH_2)m - C - O - (CH_2CH_2O)zR$$

wherein

R= alkyl or aliphatic, normal or branched, saturated or unsaturated, C8 - C30;

R'=alkyl, normal or branched, C1 - C24 or aliphatic, normal or branched, saturated or unsaturated, C8 - C30;

m=0 - 100, more specifically 0 - 10, and still more specifically 1 - 6; x=0 - 500, more specifically 0 - 20, and still more specifically 0 - 10;

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y=2 - 1000, more specifically 2 - 200, and still more specifically 6 - 100; z=0 - 1000, more specifically 0 - 200, and still more specifically 0 - 100.

In addition to the softening agents mentioned specifically above, any of a variety of other chemicals known to soften or lubricate a tissue can also be used in accordance with the present invention. Examples of such chemicals can include, but are not limited to, fatty dialkyl quaternary amine salts, mono fatty alkyl tertiary amine salts, primary amine salts, imidazoline quaternary salts, silicone quaternary salt and unsaturated fatty alkyl amine salts. Other suitable chemicals include, long-fatty acid derived compounds including esters, salts, soaps, and quaternary ammonium compounds, polyols with hydrophobic and hydrophilic characteristics, etc. Still other suitable softening agents are disclosed in U.S. Patent Nos. 5,529,665 to Kaun and 5,558,873 to Funk, et al., which are incorporated herein in their entirety by reference thereto. In particular, Kaun discloses the use of various cationic silicone compositions as softening agents.

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One commercially available softening agent is available from the Quaker Chemical Company of Conshohocken, Pennsylvania, under the trade designation "Quaker 2008." The addition of certain softening agents in the amount of, for example, 1 to 4 percent, by weight, of the composite also appears to reduce the measured static and dynamic coefficients of friction and improve the abrasion resistance of the continuous filament-rich side of the composite fabric. In this embodiment, the softening agent can be added to the fiber slurry in an amount from about 0.2% to about 1% by weight, based on the total weight of fibers present within the slurry.

In one embodiment, the softening agent can be a quaternary lotion, such as a quaternary silicone spray. For instance, the composition can include a silicone quaternary ammonium chloride. One commercially available silicone glycol quaternary ammonium chloride suitable for use in the present invention is ABIL SW marketed by Goldschmidt Chemical

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Company of Ess n, Germany. Quaternary silicone compositions can be particularly useful as softening agents in the present application because they bond with the cellulosic fibers contained within the base web. By bonding to the cellulosic fibers, the composition does not transfer onto the user's skin when the tissue product is used. In one embodiment, the softening agent is applied to one side of the layer in an amount from about 0.4% to about 2% by weight and particularly from about 0.4% to about 1.4% by weight, based upon the weight of the layer.

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In an alternative embodiment, the softening agent can also contain anti-microbial agents for destroying germs that come in contact with the layer. For instance, one particular commercially available softening spray having anti-microbial properties is DOW 5700 marketed by the Dow-Corning Corporation of Midland, Michigan. DOW 5700 is a silicone quaternary spray that contains anti-microbial agents. In a further embodiment, the softening agent can also include a fragrance or odor maskant. The fragrance can be added to the softening agent in order to mask the smell of the silicone composition or can be added to give the resulting tissue product a desired and aesthetic scent.

Besides the above mentioned materials, it should be understood that any other additive, agent, or material can be added to a tissue of the present invention, if desired. For example, various additives can be applied to a tissue of the present invention to aid in retention of the softening agent. Examples of such retention aids are described in U.S. Patent No. 5,830,317 to <u>Vinson et al.</u>, which is incorporated herein in its entirety by reference thereto.

Unfortunately, the use of even small amounts of a softening agent in the tissue can sometimes cause excessive degradation of the web surface(s), thereby resulting in significant increases in slough and lint production. This degradation is believed to be at least partially due to the propensity of the softening agent to compete with the bonding agent for

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"bonding sites" on an outer layer of a tissue. In particular, a softening agent may occupy "bonding sites" normally utilized by the bonding agent. As used herein, a "bonding site" generally refers to a substituent of a fiber to which various materials can bond. For example, common bonding sites for cellulosic fibers can include hydroxy substituents to which cationic softening and bonding agents are attracted. Thus, although a softening agent can provide a soft, lubricated surface feel, it can also cause surface degradation by lessening the ability of the bonding agent to bond to the fibers.

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As such, in accordance with the present invention, various mechanisms can be employed to allow the tissue to have a soft, lubricated feel without resulting in substantial surface degradation, slough and lint production. In particular, one or both of the outer layers of the tissue can be appropriately configured to have an increased number of bonding sites. It is believed that the increased number of bonding sites can allow for bonding of the softening agent to the fibers without significantly interfering with the bonding of the bonding agent to the fibers.

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By providing such an increased number of bonding sites, it has been discovered that the outer layers of a tissue can handle increased loads of a softening agent without resulting in substantial losses in strength. In fact, it has been discovered that a tissue produced according to the present invention can be applied with a softening agent in an amount from about 1 kilogram per metric ton of fiber weight (kg/MT) to about 60 kg per metric ton of fiber weight, and more particularly between about 10 kg/MT to about 35 kg/MT. Moreover, it has also been discovered that the tissue can retain at least about 75% of the softening agent, and more particularly between about 80% to about 96% of the softening agent.

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In accordance with the present invention, one or both of the outer layers can comprise any of a variety of materials capable of providing a

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sufficient number of bonding sites to allow a soft, yet strong tissue to be formed therefrom. In addition to providing increased bonding sites, the fibers of the outer layer(s) can also prevent lint from escaping the center of the tissue and further enhance the strength of the tissue.

5

In this regard, one embodiment of the present invention includes the use of one or more outer layers that contain at least some fibers having a "high-average length". As stated above, the phrase "high-average length" generally refers to fibers having an average fiber length greater than about 1.2 mm, and usually from about 1.5 mm to about 6 mm. When utilized, fibers having a high-average length can provide a tissue product that is not only soft and strong, but also low in slough and lint production. For instance, softwood fibers, such as northern and southern softwood kraft fibers, are some examples of suitable high-average length fibers that can be used in outer layer(s) of the present invention.

15

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In some embodiments, to further enhance the ability of such fibers to be sufficiently soft and strong, the high-average length fibers can also be fibrillated to increase the number of bonding sites available to the softening agent and/or bonding agent. Fibrillation generally refers to the random splitting of fibers into minute fibrous elements or fibrils. By fibrillating a fiber, its surface area can, in some instances, be dramatically increased so as to provide an increased number of bonding sites.

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Fibrillation can be accomplished according to any of a variety of well-known methods. For example, fibrillation can be accomplished through mechanical agitation, such as described in U.S. Patent Nos. 4,608,292 to <u>Lassen</u> or 4,701,237 to <u>Lassen</u>, which are incorporated herein in their entirety by reference thereto. Moreover, fibrillation can also be accomplished through other methods, such as by contacting the fibers with a fibrillation-inducing medium. For instance, U.S. Patent Nos. 5,759,926 to <u>Pike et al.</u>, 5,895,710 to <u>Sasse et al.</u>, and 5,935,883 to <u>Pike</u>,

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which are incorporated herein in their entirety by reference thereto, describe a variety of fibrillation-inducing mediums that can be used in the present invention, such as hot water, steam, air/steam mixtures, etc.

When the fibers are fibrillated, as described above, the extent of fibrillation can generally vary. In fact, any amount of fibrillation can provide at least some increase in the number of available bonding sites, and thus provide increased strength and softness. Nevertheless, in most embodiments, it is typically desired that the high-average length fibers are fibrillated to an extent such that the resulting fibers have a Canadian Standard Freeness ("CSF") (TAPPI T227m-58) between about 400 to about 800, and more particularly, between about 500 CSF to about 700 CSF. Canadian Standard Freeness is generally a measurement of the drainage properties of fibers as a result of refinement. For example, 800 CSF represents a relatively low amount of pulp refinement, while 400 CSF represents a relatively high amount of pulp refinement.

In addition to, or in combination with, the use of fibrillated fibers, fibers having a low-average length can also be combined or blended with fibers having a high-average length (fibrillated or un-fibrillated) to provide the desired increase in the number of available bonding sites. For example, in one embodiment, eucalyptus fibers having a low-average length can be combined with softwood fibers having a high-average length. Moreover, in another embodiment, eucalyptus fibers can be combined with softwood fibers, some of which have been fibrillated as described above. When utilized, low-average length fibers can generally be incorporated into the outer layer(s) in any desired amount. Typically, a fiber blend used in an outer layer of the present invention contains about 50% to about 95% by weight of low-average length fibers, and more particularly between about 60% to about 90%.

A tissue of the present invention can generally be formed according to a variety of papermaking processes known in the art. In particular, it should be understood that the present invention is not limited to any particular papermaking process. In fact, any proc ss capable of forming a tissue having multiple layers can be utilized in the present invention. For example, a papermaking process of the present invention can utilize creping, embossing, wet-pressing, through-drying, through-dry creping, uncreped through-drying, double creping, as well as other steps in forming the multi-layered paper web. For example, in one embodiment of the present invention, the tissue can be formed using an uncreped through-drying technique, such as disclosed in U.S. Patent Nos. 5,048,589 to Cook, et al. and 5,399,412 to Sudall, et al., which are incorporated herein in their entirety by reference thereto. Still other methods of forming tissues are also described and disclosed in U.S. Patent No. 5,129,988 to Farrington, Jr. and in U.S. Patent No. 5,494,554 to Edwards, et al., which are both incorporated herein in their entirety by reference thereto.

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Tissues, such as facial tissues, made according to the present invention provide many advantages and benefits over conventional tissue products. The facial tissues have improved facial softness, low surface friction, low lint production, low slough, high wet strength, and good tear resistance. In particular, due to the number of bonding sites readily available to both the bonding agent and softening agent, high loads of softening agent can be handled by the tissue without causing substantial slough and lint production.

The present invention may be better understood with reference to the following examples:

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## **EXAMPLE 1**

The ability of a tissue of the present invention to effectively retain a softening agent was demonstrated. In general, to determine the retention of the softening agent, a sample of tissue having a basis weight of about 18.5 pounds per ream was weighed and extracted in a sealed container for a given amount time on a flatbed shaker at ambient

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conditions. After the extraction, the tissue was removed and the extract was allowed to settle. The extract was then analyzed by an ultraviolet spectrometer. After the percent extracted was calculated, the add-on percentage was determined by an add-on correlation curve, such as described below.

## Construction of Add-On Correlation Curve

Initially, 5.00 grams of the tissue was weighed out for each replicate (three samples for each add-on level and three untreated samples) and placed into a sealable container. Four levels of add-on (i.e., 0.1, 0.3, 0.8, and 1.0%) were utilized to generate the curve. Thus, three blank samples and three samples for each add-on level were tested, resulting in 15 total samples.

Two sets of spiking solutions were then prepared to supply the required add-on levels (1000 and 5000 ppm). Specifically, 1.250 and 6.250 grams of the C-6001 softening agent were placed into 50 ml beakers. Thereafter, the softening agents were combined with distilled water and transferred to a 1000 ml flask. The solutions were then shaken and allowed to dissolve. The add-on levels were formed as follows:

	Add-on Level	1000ppm	5000ppm
20	0.1%	5mL	_
	0.3%	15mL	_
	0.8%	-	8mL
	1.0%	_	10mL

Once formed, the spike solution was applied to the tissue samples and dried for 48 hours in a 60 degree Celsius oven. Thereafter, 100 ml of methanol was added to the dried, spiked tissue samples and sealed in the containers. The solutions were then placed in a flatbed shaker and extracted for a given amount of time (i.e., ½ hour to 16 hours). The tissue samples were then removed so that the extract could settle. A transfer pipette was used to deliver a certain amount of the solution for UV

absorbance readings at 238 nm wavelength. A 1/10 dilution was required for some add-on tissue samples to obtain an adequate reading. Blanks were read with and without this dilution. A 1/10 dilution reading was used for 1/10 dilution samples and a no-dilution reading was used for the no-dilution samples. For each add-on level, the mean absorbence readings for each of the 3 replicates was subtracted from the value read from the blanks.

The percent extracted was then calculated from the ppm reading from the standard curve (imidazoline). In particular,

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## No Dilution:

% Extracted = ppm reading X 0.1 X 100/5000 1/10 Dilution:

% Extracted - ppm reading X 0.1 X 10 X 100/5000

An Add-on Correlation curve was then constructed with the percent extracted values. The best fitting curve (first or second order) was selected.

#### Sample Test

After developing the add-on correlation curve, replicates of three multi-layered tissue samples having basis weights of about 18.5 pounds per ream were produced and applied with a softening agent in accordance with the present invention. Each sample contained an outer layer of varying blends of "Longlac-19", which is available from Kimberly-Clark Corporation, and eucalyptus fibers. A Witco C-6001 imidazoline-based softener was applied to each sample in an amount of 0.4% by weight, based upon the weight each respective paper web.

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After being applied with the imidazoline-based softener, each sample was then tested using the above-mentioned procedure to determine the total amount of softener that was retained on the tissue upon application. Specifically, 5.00 grams of the softening agent treated tissue sample was placed in a specimen container, to which 100 ml of

methanol was added. The specimen containers were placed on the flatbed shaker and extracted for the same amount time as the spike and recovery samples. The tissue was removed and the extracts were allowed to settle. The extracts were then read at 238 nm wavelength, wherein the sample reading was subtracted from the blank absorbance reading. The "ppm" of the softening agent was then used to calculate the percent extracted value. Using the Add-on correlation curve, the percent add-on was then calculated from the percent extracted value. The retention efficiency was then calculated, i.e. the percentage of softener that was retained upon the tissue web. The results are given below in Table 1:

**TABLE 1: Imidazoline Softener Retention** 

Eucalyptus Fibers (wt.	Longlac-19 Fibers	Imidazoline Target (wt.	Imidazoline Detected	Retention Efficiency
%)	(wt.%)	(%)	(wt. %)	(%)
100	0	0.4	0.318	79.5
50	50	0.4	0.326	81.5
30	70	0.4	0.383	95.8

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As indicated by Table 1, the ability of a tissue to retain a softening agent is enhanced by the use of high-average length fibers in a fibrous blend with low-average length fibers.

#### **EXAMPLE 2**

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The ability of a tissue of the present invention to effectively retain a softening agent and to be applied with a softening agent without a substantial loss in strength was demonstrated. Twelve tissue samples having a basis weight of about 18.5 pounds per ream were produced having an outer layer of fibrillated "Longlac-19" fibers, which are available from Kimberly-Clark Corporation, in accordance with the present

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invention. Specifically, the fibers of each sample were fibrillated at varying degr es using conventional refining machinery such that three of the tissue samples had a Canadian Standard Freeness of 681, four of the tissue samples had a Canadian Standard Freeness of 600, and five of the tissue samples had a Canadian Standard Freeness of 525, as determined by TAPPI Standard Method T227m-58. A Witco C-6027 imidazoline-based softener softening agent was then applied to each sample at varying levels as indicated in Figure 1. After being applied with the imidazoline-based softener, each sample was then tested to determine the total amount of softener that was retained on the tissue upon application in accordance with the procedures set forth in Example 1.

In addition, the strength of each sample applied with the imidazoline-based softener was also tested. In particular, the geometric mean tensile strength ("GMT") was calculated as the square root of the product of the machine direction tensile strength and the cross-machine direction tensile strength. The units of GMT strength are grams per 3 inches of sample width, but are simply referred to herein as "grams". Tensile strengths were determined in accordance with TAPPI test method T 494 om-88 using flat gripping surfaces, a specimen width of 3 inches, a length of 6 inches, and a crosshead speed of about 10 inches per minute.

The results are illustrated in Figure 1. As shown, for example, the paper web containing fibers having a Canadian Standard Freeness of 525 achieved a high softening add-on level without a substantial loss in tensile strength.

**EXAMPLE 3** 

The ability of a tissue of the present invention to effectively retain a softening agent and to be applied with a softening agent without a substantial loss in strength was demonstrated. Two sets, each containing three tissue samples having basis weights of about 18.5 pounds per ream, were produced and applied with a softening agent in accordance

with the present invention. One set of samples contained an outer layer of 100% eucalyptus fibers and the other set of samples contained an outer layer of 50% eucalyptus fibers and 50% "Longlac-19" fibers, which are available from Kimberly-Clark Corporation. A Witco C-6001 imidazoline-based softener was then applied to each sample at varying levels.

After being applied with the imidazoline-based softener, each sample was then tested as set forth in Example 1 to determine the total amount of softener retained on the tissue. In addition, the strength of each sample applied with the imidazoline-based softener was also tested as set forth in Example 2.

The results are illustrated in Figure 2. As shown, the paper web containing eucalyptus and "Longlac-19" fibers had the highest extracted softening level (i.e., retention), while the paper web containing only eucalyptus fibers had the lowest retention of the softening agent.

Moreover, as shown, the paper web containing eucalyptus and "Longlac-19" fibers had the highest GMT value, while the web containing only eucalyptus fibers has the lowest GMT value.

### **EXAMPLE 4**

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The ability of a tissue of the present invention to effectively reduce slough was demonstrated. Two tissue samples having basis weights of about 18.5 pounds per ream were produced, wherein one sample contained an outer layer having only eucalyptus fibers and the other sample contained an outer layer having 50% "Longlac-19" fibers, which are available from Kimberly-Clark Corporation, and 50% eucalyptus fibers. A Witco C-6001 imidazoline-based softener was applied to each sample in an amount of 8 kilogram per metric ton of each respective paper web.

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After being applied with the imidazoline-based softener, each sample was then subjectively tested by a group of panelists to determine

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the amount of dry and wet slough generated by the tissues. Specifically, for evaluating dry slough, each panelist rubbed their thumb against the tissue samples and visually assessed the slough generated. Moreover, for evaluating wet slough, each panelist rubbed their wetted thumb against the tissue samples and visually assessed the slough generated. The tissue sample containing only eucalyptus fibers was observed to have more dry and wet slough than the tissue sample containing eucalyptus fibers and Longlac-19 fibers.

Although various embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those of ordinary skill in the art without departing from the spirit or scope of the present invention, which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.

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# WHAT IS CLAIMED IS:

1. A soft tissue comprising:

a first and second outer layer, wherein said first layer comprises a fibrous material, said fibrous material comprising fibers having a high-average length, wherein at least a portion of said high-average length fibers are fibrillated;

a softening agent applied to said first layer, said softening agent having at least some affinity to said fibrous material of said first layer.

- 2. A soft tissue as defined in claim 1, wherein said high-average length fibers have an average length between about 1.5 mm to about 6 mm.
- 3. A soft tissue as defined in claim 1, wherein said high-average length fibers comprise cellulosic fibers.
- 4. A soft tissue as defined in claim 3, wherein said cellulosic fibers comprise softwood fibers.
- 5. A soft tissue as defined in claim 1, wherein said fibrillated highaverage length fibers have a Canadian Standard Freeness value between about 400 to about 800.
- 6. A soft tissue as defined in claim 1, wherein said fibrillated highaverage length fibers have a Canadian Standard Freeness value between about 500 to about 700.
- 7. A soft tissue as defined in claim 1, wherein said fibrous material further comprises fibers having a low-average length.
- 8. A soft tissue as defined in claim 7, wherein said low-average length fibers comprise from about 50% to about 95% by weight of said fibrous material.
- 9. A soft tissue as defined in claim 7, wherein said low-average length fibers comprise from about 60% to about 90% by weight of said fibrous material.
  - 10. A soft tissue as defined in claim 7, wherein said low-average

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length fibers comprise eucalyptus fibers.

- 11. A soft tissue as defined in claim 7, wherein said low-average length fibers have an average length from about 0.7 mm to about 1.2 mm.
- 12. A soft tissue as defined in claim 1, wherein said fibrous material is applied with a bonding agent.
- 13. A soft tissue as defined in claim 1, wherein said softening agent comprises an imidazoline compound.
- 14. A soft tissue as defined in claim 1, wherein said softening agent is applied in an amount between about 1 kilogram per metric ton to about 60 kilograms per metric ton.
- 15. A soft tissue as defined in claim 1, wherein said softening agent is applied in an amount between about 10 kilograms per metric ton to about 35 kilograms per metric ton.
  - 16. A soft tissue comprising:

a first and second outer layer, wherein said first layer comprises a fibrous material, said fibrous material comprising fibers having a high-average length and fibers having a low-average length; and

a softening agent applied to said first layer, said softening agent having at least some affinity to said fibrous material of said first layer.

- 17. A soft tissue as defined in claim 16, wherein said high-average length fibers have an average length between about 1.5 mm to about 6 mm.
- 18. A soft tissue as defined in claim 16, wherein said high-average length fibers comprise cellulosic fibers.
- 19. A soft tissue as defined in claim 18, wherein said cellulosic fibers comprise softwood fibers.
- 20. A soft tissue as defined in claim 16, wherein at least a portion of said high-average length fibers are fibrillated.
- 21. A soft tissue as defined in claim 20, wherein said fibrillated high-average length fibers have a Canadian Standard Freeness value

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between about 400 to about 800.

- 22. A soft tissue as defined in claim 20, wherein said fibrillated high-average length fibers have a Canadian Standard Freeness valu between about 500 to about 700.
- 23. A soft tissue as defined in claim 16, wherein said low-average length fibers comprise between about 50% to about 95% of said fibrous material.
- 24. A soft tissue as defined in claim 16, wherein said low-average length fibers comprise from about 60% to about 90% by weight of said fibrous material.
- 25. A soft tissue as defined in claim 16, wherein said low-average length fibers comprise eucalyptus fibers.
- 26. A soft tissue as defined in claim 16, wherein said low-average length fibers have an average length from about from about 0.7 mm to about 1.2 mm.
- 27. A soft tissue as defined in claim 16, wherein said fibrous material is applied with a bonding agent.
- 28. A soft tissue as defined in claim 16, wherein said softening agent comprises an imidazolinium compound.
- 29. A soft tissue as defined in claim 16, wherein said softening agent is applied in an amount between about 1 kilogram per metric ton to about 60 kilograms per metric ton.
- 30. A soft tissue as defined in claim 16, wherein said softening agent is applied in an amount between about 10 kilograms per metric ton to about 35 kilograms per metric ton.
  - 31. A soft tissue comprising:

an inner layer positioned between a first and second outer layer, wherein said first and said second outer layers comprise a fibrous material, said fibrous material comprising softwood pulp fibers, wherein at least a portion of said softwood pulp fibers are fibrillated, said fibrillated

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softwood pulp fibers having a Canadian Standard Freeness value between about 400 CSF to about 800 CSF.

- 32. A soft tissue as defined in claim 31, wherein said fibrillated softwood fibers have a Canadian Standard Freeness value between about 500 to about 700.
- 33. A soft tissue as defined in claim 31, wherein said fibrous material further comprises eucalyptus fibers.
- 34. A soft tissue as defined in claim 33, wherein said softwood fibers comprise between about 5% to about 50% by weight of said fibrous material.
- 35. A soft tissue as defined in claim 31, wherein said inner layer comprises a fibrous material, wherein said fibrous material of said inner layer comprise softwood pulp fibers.
- 36. A soft tissue as defined in claim 31, wherein one of said or said second outer layers is applied with a softening agent.
  - 37. A soft tissue comprising:

an inner layer positioned between a first and second outer layer, wherein said first and said second outer layers comprise a fibrous material, said fibrous material comprising softwood pulp fibers and eucalyptus fibers, said softwood fibers comprising between about 5% to about 50% by weight of said fibrous material.

- 38. A soft tissue as defined in claim 37, wherein at least a portion of said softwood pulp fibers are fibrillated.
- 39. A soft tissue as defined in claim 37, wherein said inner layer comprises a fibrous material, wherein said fibrous material of said inner layer comprise softwood pulp fibers.
- 40. A soft tissue as defined in claim 37, wherein one of said or said second outer layers is applied with a softening agent.
- 41. A method of forming a soft tissue, said method comprising the step of:

providing a first layer of fibrous material;
providing a second layer of fibrous material;
increasing the number of bonding sites of said first lay r of fibrous material; and

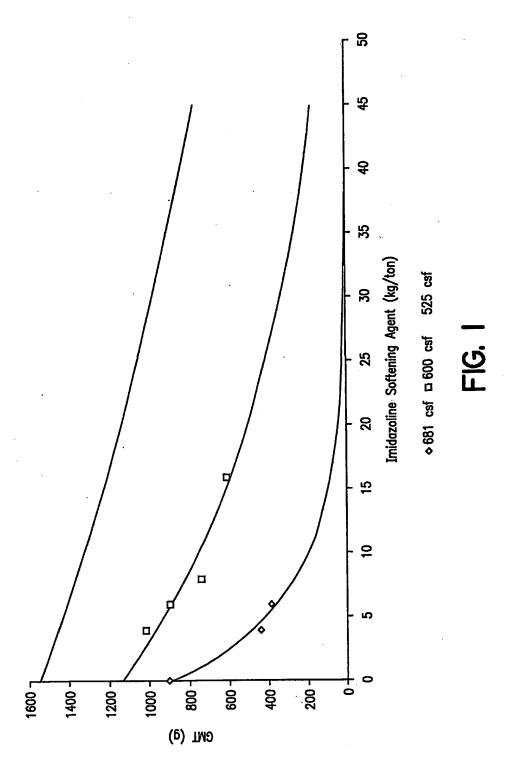
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applying a softening agent to said first layer of fibrous material, said softening agent having at least some affinity to said fibrous material.

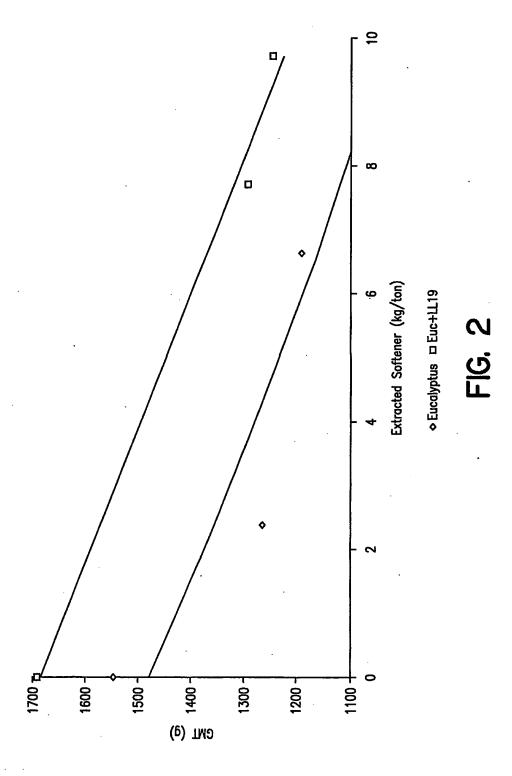
42. A method of forming a soft tissue as defined in claim 41, wherein said number of bonding sites is increased by providing said first layer with fibrillated, high-average length fibers.

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43. A method of forming a soft tissue as defined in claim 41, wherein said number of bonding sites is increased by providing said first layer with high-average length and low-average length fibers.



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